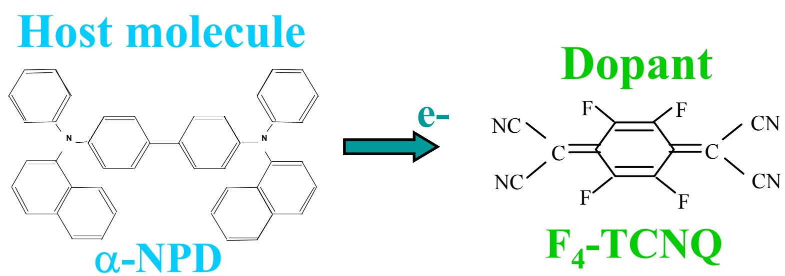
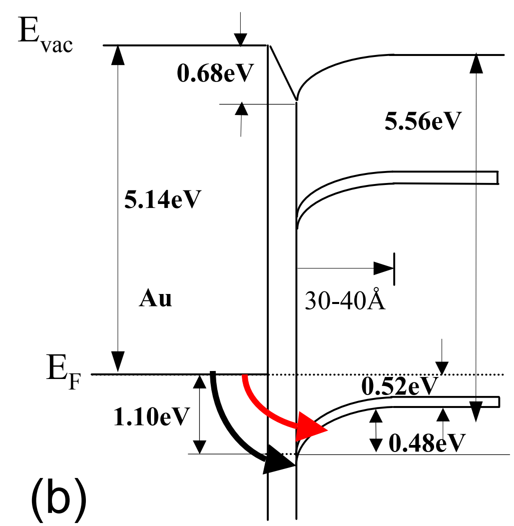
Injection enhancement via controlled, spatially-resolved, electrical doping of an organic molecular material

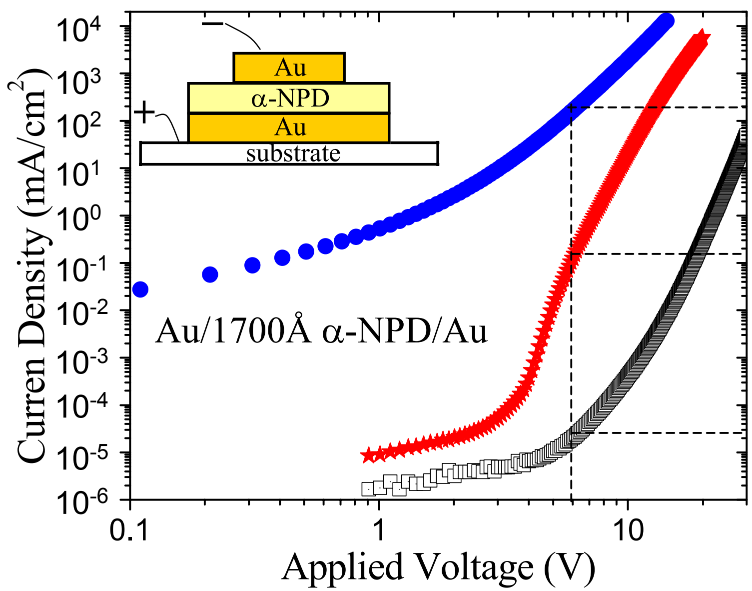


(a)

α-NPD:3% F4–TCNQ / Au



(b)



(c)

- □ **Au/1700Å undoped α -NPD/Au**
- ★ **Au/80Å α-NPD:4% F_4-TCNQ + 1620Å pure α -NPD/Au**
- ● **Au/1700Å α -NPD:4% F_4-TCNQ/Au**

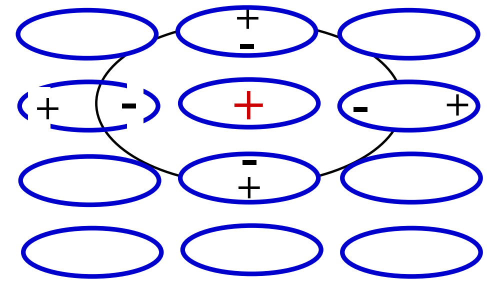
Electrical doping of organic molecular films is a very important way to increase charge carrier injection at interfaces. Given the fast growing field of organic micro- and optoelectronic devices, considerable interest is given to schemes that improve carrier injection, and thus increase device efficiencies and decrease drive voltages.

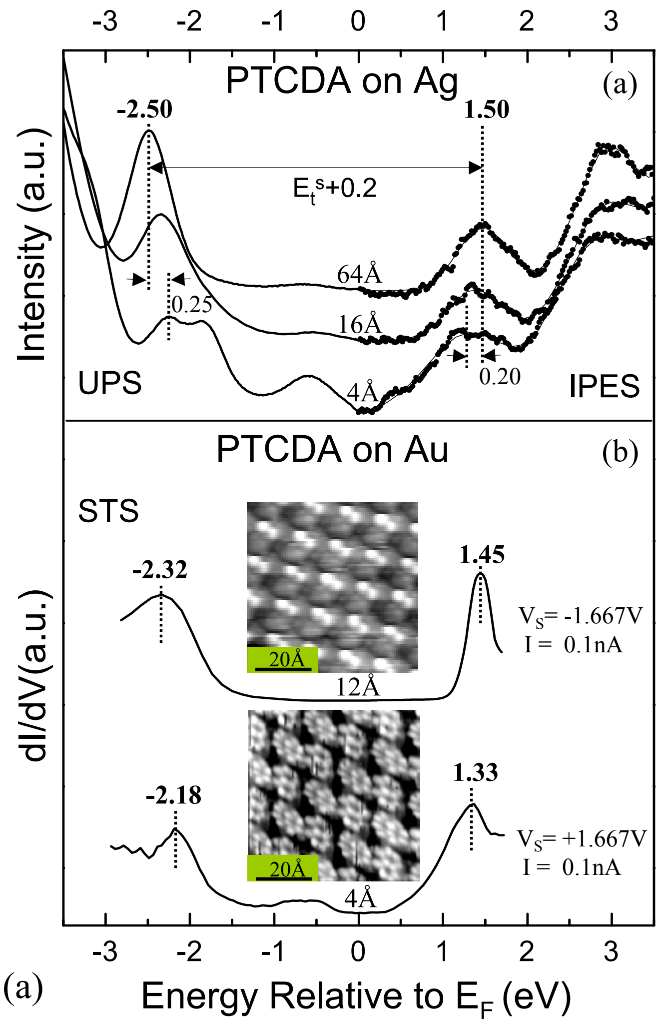
Heavy doping of a semiconductor interface produces a narrow depletion region, which allows tunneling of charge carriers through the barrier (red arrow in (b)). The "effective injection barrier" is therefore considerably reduced with respect to the true barrier (black arrow in (b).

We have recently demonstrated that the widely used hole transport molecular materials ZnPc (zinc phthalocyanine) [1,2] and α–NPD (N,N'-diphenyl-N,N'-bis(l-naphthyl)-l,l'biphenyl-4,4''diamine) [3] can be efficiently p-type doped with the strong electron acceptor F_4-TCNQ (tetrafluorotetracyanoquinodimethane) (Fig.(a)). Using our unique combination of direct and inverse photoemission spectroscopy, we show that the doping mechanism corresponds to the transfer of a full electron from the highest occupied molecular orbital of the α–NPD host to the lowest unoccupied molecular orbital of F_4-TCNQ. The incorporation of the dopant molecules is achieved via co-evaporation of α–NPD and F_4-TCNQ. Fig. (b) shows the measured electronic structure and "band bending" in a film of α–NPD:4%F_4-TCNQ deposited on a gold surface. The thickness of the depletion region is 3-4 nanometers, and the molecular level bending is 0.48 eV. In addition, we are able to control the incorporation of dopant over film thicknesses of the order of 10 nanometers. Fig. (c) shows the current-voltage characteristics corresponding to the injection of holes from the Au substrate (see inset) into α–NPD, when the film is undoped (□); doped over only 8 nm from the interface (★); homogeneously doped throughout the film (•). Interface doping increases the current by nearly 4 orders of magnitude via tunneling! Homogeneous doping additionally increases the film conductivity.

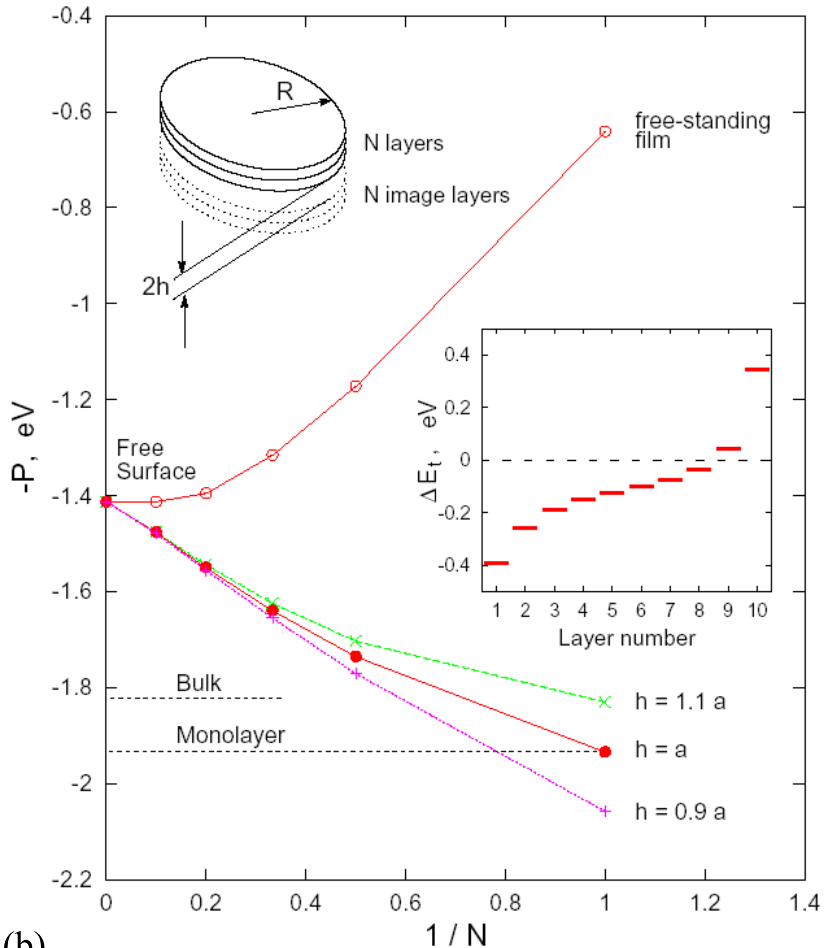
1. W. Gao and A. Kahn, Appl. Phys. Lett., **79**, 4040 (2001)
2. W. Gao and A. Kahn, Organic Electronics (accepted for publication; in press; 2002)
3. W. Gao and A. Kahn, J. Appl. Phys. (submitted)

Electronic Polarization at the Surface of Molecular Films





(a)



(b)

Electrical polarization dominates the physics and transport of charge carriers in molecular solids. When a charge (electron or hole) in placed on a molecule, the electron distribution of the molecule and of its neighbors is perturbed (schematic in upper right corner). The electronic (and atomic) rearrangement, also known as polarization, “screens” the excess charge and stabilizes it. Understanding and evaluating polarization and its effect on molecular levels is exceedingly important in order to define “transport” levels, i.e. energy levels at which single particles (electrons or holes) are transported through the organic materials.

We present here the first experimental evidence and quantitative assessment of varying polarization at the surface of a film of PTCDA molecules (perylenetetracarboxylic dianhydride) as a function of film thickness and, thus, surface-to-metal-substrate distance. The experimental evidence is obtained via ultra-violet and inverse photoemission spectroscopies (UPS/IPES) for PTCDA/silver (upper panel of Fig.(a)) and scanning tunneling spectroscopy (STS) for PTCDA/gold (lower panel of Fig. (a)). The STS curves are taken on 1 and 3 molecular layer films exhibiting high molecular order. The UPS/IPES and STS curves show the highest occupied and lowest unoccupied molecular orbitals and the energy gap. In both cases, these electronics states shift by ~0.2-0.3 eV *away* from the center of the gap with increasing film thickness, in accord with decreasing *polarization*.

These measurements are beautifully confirmed by self-consistent and fully converged calculations (Fig. (b)) performed for films of N molecular planes placed on a metal substrate, with a distance h between the metal surface and the interface molecular plane. The calculations yield the total polarization P (electron + hole) in the bulk (1.82 eV), at the surface of a monolayer film on the metal surface ((1.92 eV) as well as at the surface of an infinitely thick film (N large) (1.41 eV). The inset of Fig. (b) shows the impact of polarization on the single-particle energy gap of a 10 molecular plane films, from the interface (layer number = 1) to the surface of the film.

E. Tsiper, Z. Soos, W. Gao and A. Kahn, Chem. Phys. Lett. (2002) (in press).

Princeton Center For Complex Materials Curriculum Support and Teacher Training

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PCCM Science Curriculum Support Project (SCSP)

SCSP began in January 11 1999 with a K-12 education workshop for Princeton Materials and Environmental scientists. PCCM faculty experienced some of the exciting advances in pre-college science education. This led to the a new synergy between school districts and PCCM/PMI scientists to improve elementary school science education. 3 STC and 3 FOSS kits were chosen for support. Teams of scientists and elementary/ middle-school teachers worked to develop web resources that support hands-on, inquiry-centered science curricula.

The kits supported so far are:

Chemical Tests (STC)

Earth Materials (FOSS)

Electric Circuits (STC)

Magnets and Motors (STC)

Mixtures and Solutions (FOSS)

Water (FOSS)

Water on Earth (Lawrence Intermediate School)

These are available at our education web site:

http://www.princeton.edu/~pccm/outreach/scsp/index.html

Each team, focusing on one curriculum unit, creates a set of resources for current and future teachers using these units. These resources are placed on our web site. Support resources on the site include:

•Scientific background content

•Notes and practical tips to help teachers carry out projects

•Lists of additional readings, related web sites and videos for both teachers and students

•Extensions: projects or activities to challenge students or for the kit-recycling periods

We have developed the PCCM Electricity,magnets and motors kit and training program for districts that have not adopted the Electric Circuits and Magnets and Motors kits. 16 local school districts were provided with these complementary kits and a full day training program. The program will continue in 2002/2003 academic year.

Curriculum Outline: MORNING SESSION

(Emphasis throughout on ENERGY flow and conversion)

1. Electric circuit

- circuit loop; - battery (source of energy; give the "lead-acid battery" demo using the kit?)

- lamp ("consumer" of energy); - electron;

- current; - voltage; - switch

- conductor (and insulator); - resistance (resistor); - voltmeter (measure voltage, current, resistance)

2. Parallel/series combination of 2 batteries and 2 light bulbs

3. Ohm's law

- use a fixed resistor (R = 1000 Ohm), and measure current (I) and voltage (V) for 1, 2, and 4 batteries, plot I vs. V and verify V = I.R

- measure I and V for different size resistors (100, 330, and 1000 Ohms) and verify again V = I.R. (First, measure resistances using the ohmmeter, then set up the circuit and measure I and V.)

4. Parallel/series resistors

- measure the resistance of pairs of resistors in parallel/series (using ohmmeter)

5. Set up a circuit with a light bulb and a diode in series

6. Use the hand-crank generator instead of the battery in a couple of circuits (e.g., with the light bulb). Will learn how the generator works in the afternoon.

- talk about different types of ENERGY and CONVERSION: chemical (battery) or mechanical (generator) -> electrical -> heat -> light

(Remind teachers that in the generator case it is actually the chemical energy in our body that gets converted to mechanical energy.

- can "experience" that generating energy costs "effort"! (First, crank the generator without hooking up to anything. Then hook up to one light bulb. Then to two bulbs in series, etc.)

- Now run the generator in reverse (i.e., hook to a battery) to show:

chemical (battery) -> electrical -> mechanical

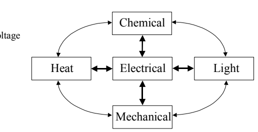
(remind teachers about the "motor" in toys, etc.)

PCCM Kit's contents:

-voltmeter (volts, amps, ohms)
-size D batteries (2) and battery holder
-knife switches (2)
-light bulbs and sockets (2)
-resistors (100, 330, and 1000 Ohms, 2 of each)
-diode (one regular and one LED)
-6" bar magnets (2)
-compass
-simple motor kit
-small motor
-hand-crank generator
-wire (about 6' of single conductor)
-screw driver
-wire cutter and stripper
-sand paper
-screw and wire (for electromagnet)
-tooth pick
-graphite rod (pencil "lead")
-paper clips (5 or 6 in each kit)
-graph paper

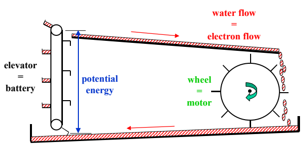
Key concepts for electrical circuits

- Electrical circuits
  - Electron
  - Conductor
  - Insulator
  - Current
  - Battery and Voltage
  - Switch
  - Resistance
  - Energy



Conceptual Framework Electric circuits analogous to water flow

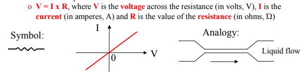
Mechanical analogy of an electric circuit with battery and motor



Potential energy given to electrons by battery is used to do work with the motor, but could also produce light in light-bulb, produce heat in radiator, etc..

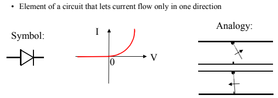
Resistance

- Element of a circuit made to oppose resistance to the flow of electrons
  - made of a "poor" conductor
  - **V = I x R**, where **V** is the **voltage** across the resistance (in volts, V), **I** is the **current** (in amperes, A) and **R** is the value of the **resistance** (in ohms, Ω)



Diode

- Element of a circuit that lets current flow only in one direction



Curriculum Outline: AFTERNOON SESSION

7. Magnet and compass:

- talk about magnets and magnetism

- deflection of compass

- "map out" magnetic field of the bar magnet using the compass and plot

8. Motor:

- magnet repels compass needle; can make needle turn by bringing magnet near and far; or turning the magnet

- moving electrons produce magnetic field; show using wire loop and generator to deflect the compass needle (use mine for demo; teachers can do it once they make their own wire loop in a few minutes).

- build an electromagnet (wrap wire around a screw to pick up paper clips)

- build a motor (using the motor kit); emphasize the simplicity: a magnet and a wire loop! Remind them again of the energy conversions.

- use and explain the "real" motor provided in the kit

9. Go back to the generator, and play/discuss more

EXTRA STUFF (if there is time; a radiometer, a solar cell, and a little speaker)

10. Other energy converting devices:

- radiometer: light -> heat -> mechanical

- solar cell: light -> electrical (-> mechanical)

- speaker: chemical (battery) or mechanical (generator) -> electrical -> mechanical (sound)